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Hydride Ion Abstraction from Titanocene Cyclic Organohydroborates, $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8, C_5H_{10}, C_8H_{14}$), as a Function of Solvent

Christine E. Plečnik, Fu-Chen Liu, Shengming Liu, Jianping Liu,
Edward A. Meyers, and Sheldon G. Shore*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Hydride abstraction reactions of titanocene cyclic organohydroborate complexes $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, C_5H_{10}, C_8H_{14}) with $B(C_6F_5)_3$ were investigated as a function of solvent. It was determined that the coordinating ability of the solvent directed the course of these abstraction reactions. The reaction in toluene, a noncoordinating solvent, produced a metathesis product, $Cp_2Ti\{(\mu\text{-}H)_2B(C_6F_5)_2\}$ (**1**), in which the cyclic organohydroborate H_2BR_2 was substituted by $H_2B(C_6F_5)_2$. In diethyl ether and THF, the salts $[Cp_2TiL_2]$ $[HB(C_6F_5)_3]$ (**2**, L = Et_2O; **3**, L = THF) consisting of titanocene cations with solvent ligands were isolated. Salt **2** is the first structurally characterized $[Cp_2TiL_2]^+$ cation containing diethyl ether solvent ligands. The diethyl ether molecules of the cation in **2** are weakly coordinated and are labilized in THF and toluene. Dissolution of **2** in THF afforded **3**. The complex $Cp_2Ti\{(\mu\text{-}H)B(C_6F_5)_3\}(OEt_2)$ (**4**) and the proposed 15-electron species $Cp_2Ti\{(\mu\text{-}H)B(C_6F_5)_3\}$ (**5**) were generated through the displacement of an ether molecule from **2** by the $[HB(C_6F_5)_3]^-$ anion in toluene. Single-crystal X-ray structures of **1**, **2**, and **3** were determined.

Introduction

Recently there has been an increased effort in the synthesis of low-valent titanocene compounds with boron-containing ligands. Such compounds can be classified as Ti(II) σ-boranes, including $Cp_2Ti(HBCat)_2$ (Cat = $o\text{-}O_2C_6H_4$) and its derivatives[1] and Ti(III) hydridoborates $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = H_2$;[2] $(C_6F_5)_2$;[3] C_4H_8, C_5H_{10}, C_8H_{14}[4]). Only a handful of such compounds have been synthesized; these complexes are structurally interesting and they exhibit potentially useful chemical properties. For instance, the Ti(II) σ-boranes have demonstrated catalytic activity in the hydroboration of alkenes and alkynes.[5]

This laboratory has been involved in expanding the number of early transition metal metallocene cyclic organohydroborates. To date, zirconocene,[6] hafnocene,[6a−c] niobocene,[4] and titanocene[4] derivatives of the cyclic organohydroborates H_2BR_2 ($R_2 = C_4H_8$,[7] C_5H_{10},[6c] C_8H_{14}[8]) have been prepared. Our interest in these types of compounds stems from their unusual reactivity with the strong Lewis acid and hydride ion abstracting reagent, $B(C_6F_5)_3$. $B(C_6F_5)_3$ has been widely utilized as an alkyl carbanion abstracting reagent[9] to generate metallocene cations[10] for olefin polymerization, but in only a few cases has $B(C_6F_5)_3$ been utilized to abstract terminal hydride from metallocenes.[11] Our latest study reveals that hydride ion abstraction from zirconocene organohydroborates likewise results in the formation of zirconocene cations (Scheme 1).[12] These reactions are influenced by several factors. Although both terminal and bridging hydrogens are present in $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, the terminal hydride is more hydridic and is preferentially abstracted by $B(C_6F_5)_3$. Furthermore, the abstraction product is a function of the coordinating ability of the solvent. Abstraction in the noncoordinating solvent benzene produces the salt, $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BC_4H_8\}_2]$ $[HB(C_6F_5)_3]$ (**A** of Scheme 1), while the reaction in the coordinating solvent diethyl ether yields the mononuclear cation in the salt, $[Cp_2Zr(OEt_2)(OEt)]$ $[HB(C_6F_5)_3]$ (**B**).

As an extension of this most recent work, we are interested in the reactions of the titanocene systems

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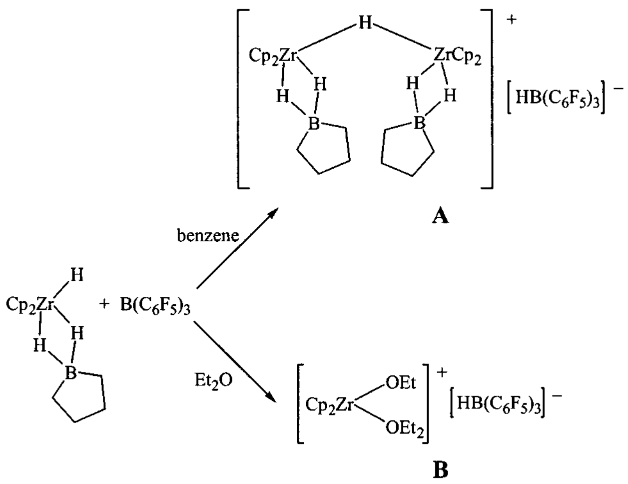
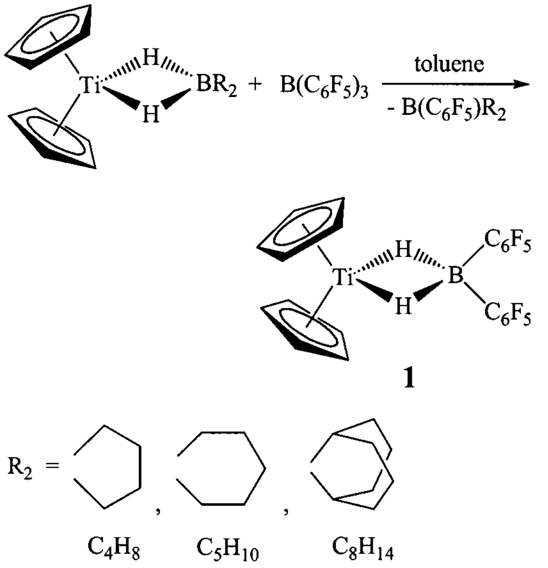
Scheme 1



$Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ (R_2 = C_4H_8, C_5H_{10}, C_8H_{14})[4] that contain only $Ti(\mu\text{-}H)_2B$ bridges, with $B(C_6F_5)_3$ as a means of generating titanocene (Ti(III)) cations, about which little is known.[13-18] It is of interest to determine whether the bridging hydrogens are sufficiently basic for abstraction and if there is a similar unique dependence on the solvent to affect the course of the reactions. In the present contribution, we report the products of these hydride abstraction reactions as a function of solvent.

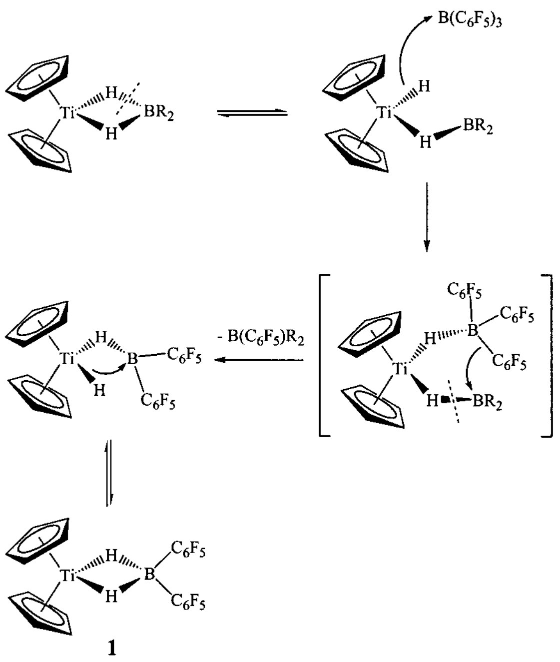
Results and Discussion

Hydride Ion Abstraction in a Noncoordinating Solvent: Formation of $Cp_2Ti\{(\mu\text{-}H)_2B(C_6F_5)_2\}$, 1. In reactions of the titanocene cyclic organohydroborates $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ (R_2 = C_4H_8, C_5H_{10}, C_8H_{14}), with $B(C_6F_5)_3$ in toluene, the unanticipated complex **1** is produced in 57 to 68% yields (reaction 1). During the course of this metathesis reaction, the organohydroborate H_2BR_2 is replaced by bis(pentafluorophenyl)hydridoborate, $H_2B(C_6F_5)_2$. Titanium activates one of the boron–carbon bonds from a pentafluorophenyl ring of $B(C_6F_5)_3$ to generate an organoborane that is believed to be $B(C_6F_5)R_2$, based on a downfield singlet (R_2 = C_4H_8, δ 81.8; R_2 = C_5H_{10}, δ 82.7; R_2 = C_8H_{14}, δ 85.0) in the ^{11}B NMR spectra. The identity of the borane, $B(C_6F_5)(C_8H_{14})$, was confirmed by GC-MS. A somewhat similar reaction was described by Marks et al. with the alkylation of Cp_3UBH_4 by BR_3 (R = C_2H_5, C_6H_5) to afford Cp_3UBH_3R and HBR_2.[19]



(1)

Scheme 2



A suggested mechanism for the formation of **1** is illustrated in Scheme 2. Terminal B–H[20] and metal–H[11,12] bonds can be abstracted as hydride ion. On the other hand, bridge hydrogens tend to be acidic in character and are less likely to be abstracted as hydride ions,[21] but double hydrogen-bridged systems of metallocene hydridoborates tend to be fluxional,[22] which was also observed in NMR studies of the organohydroborate complexes $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$,[6a,b] $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$,[6c] and $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$,[6d,23] in both coordinating and noncoordinating solvents. Therefore, it is likely that the hydrogen bridge bonds in $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ readily open and close at room temperature though this cannot be verified by NMR spectroscopy due to the paramagnetism of the Ti(III) ion. With the bridge open, a terminal hydride on titanium is accessible to $B(C_6F_5)_3$ but is not completely abstracted. It is presumed that complete abstraction does not occur without assistance from a coordinating solvent. Activation of a

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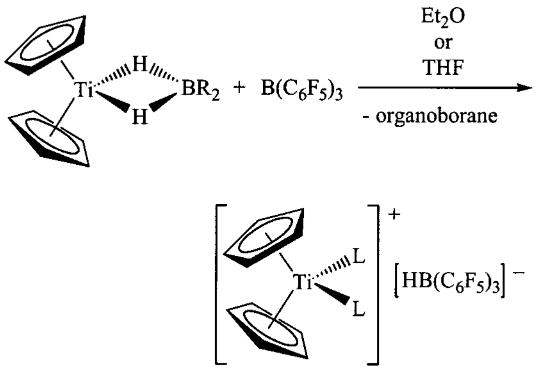
boron−carbon bond of $B(C_6F_5)_3$ then takes place, with transfer of the $[C_6F_5]^-$ moiety to BR_2. Loss of $B(C_6F_5)R_2$ occurs next with re-formation of the double hydrogen bridge. The driving force of this metathesis reaction can be discussed in terms of the relative acidities and basicities of the reactants and products. The strong Lewis acid, $B(C_6F_5)_3$, incompletely abstracts a hydride ion from the Lewis base, $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$, to produce a weaker Lewis acid, $B(C_6F_5)R_2$, and a weaker Lewis base **1**.

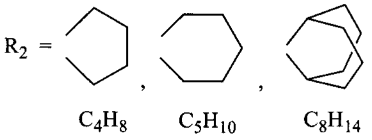
Compound **1** is paramagnetic and was identified by single-crystal X-ray analysis. It has been previously reported but prepared through different synthetic routes. Piers et al. synthesized **1** by reacting Cp_2TiR_2 (R = CH_3, CH_2Ph) with 2.5 equiv of the borane, $HB(C_6F_5)_2$.[3a] Douthwaite, on the other hand, reacted 2 equiv of the organohydroborate salt, $[(Et_2O)Li]\,[(\mu\text{-}H)_2B(C_6F_5)_2]$, with Cp_2TiCl_2 (or Cp_2TiCl in a 1:1 ratio).[3b] The latter is similar to the preparation of the starting materials, $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, C_5H_{10}, C_8H_{14}).[4] The IR and ^{19}F NMR spectra obtained in this laboratory correlate well with those of Piers et al. and Douthwaite.

Hydride Ion Abstraction in Coordinating Solvents: Formation of $[Cp_2Ti(OEt_2)_2]\,[HB(C_6F_5)_3]$, 2, and $[Cp_2Ti(THF)_2]\,[HB(C_6F_5)_3]$, 3. Hydride ion abstractions from $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, C_5H_{10}, C_8H_{14}) with $B(C_6F_5)_3$ in ether and THF solutions produce the titanocene cations $[Cp_2Ti(OEt_2)_2]^+$ and $[Cp_2Ti(THF)_2]^+$, with the $[HB(C_6F_5)_3]^-$ counteranion (reaction 2). A reasonable reaction pathway for the formation of **2** from $Cp_2Ti\{(\mu\text{-}H)_2BC_4H_8\}$ is depicted in Scheme 3. The first step would be the opening of bridge bonds to produce terminal hydrogens, either Ti−H or B−H, that are susceptible to hydride ion abstraction. When hydride ion is abstracted by $B(C_6F_5)_3$, the resulting cationic intermediate has a vacant coordination site on titanium or boron accessible to diethyl ether. Next, the displacement of the unsupported hydrogen bridge system occurs by nucleophilic attack by ether. The resulting HBC_4H_8 ring then dimerizes to the stable neutral organodiborane $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$.[24] The diborane $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$ was verified by ^{11}B NMR, with a broad unresolved triplet appearing at 28.5 ppm in ether. Unlike the reaction of $Cp_2Ti\{(\mu\text{-}H)_2BC_4H_8\}$, the reactions of $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_5H_{10}$, C_8H_{14}) with $B(C_6F_5)_3$ do not produce the parent organodiboranes $(\mu\text{-}H)_2(BC_5H_{10})_2$ and $(\mu\text{-}H)_2(BC_8H_{14})_2$ (^{11}B resonances at 26.0 and 28.3 ppm in ether, respectively), because the latter are not as stable as $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$.[24] The isolated boron-containing species have ^{11}B resonances appearing downfield as singlets at 53.7 ($R_2 = C_5H_{10}$) and 56.2 ($R_2 = C_8H_{14}$) ppm, characteristic chemical shifts for trialkyl boranes.[7b,25] Reaction of $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ with $B(C_6F_5)_3$ in THF produced **3** in 81% yield and an unidentified organoborane with an ^{11}B resonance at δ 54.0.

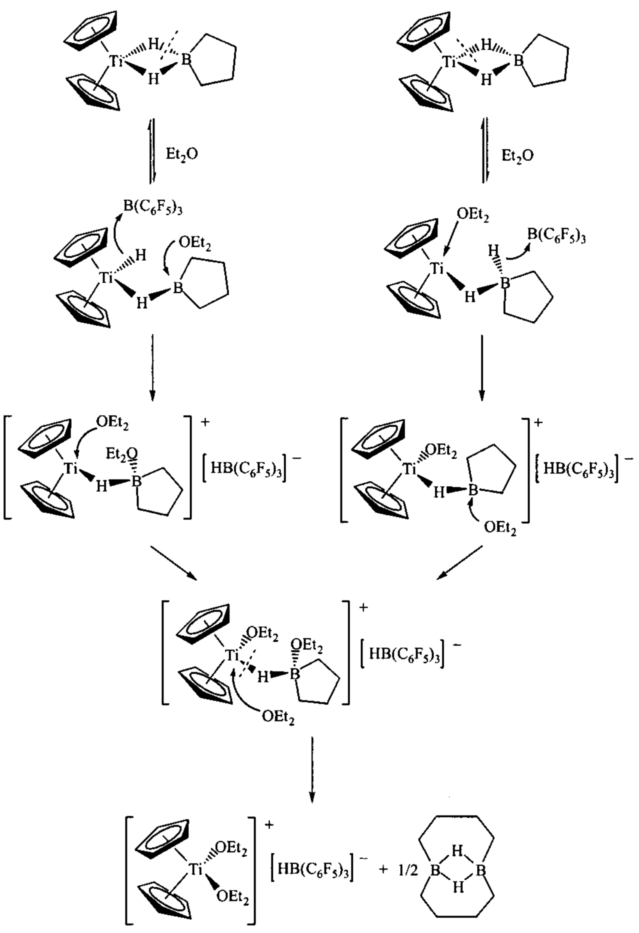


(2)

2: L = Et_2O
3: L = THF



Scheme 3



2

Since the opening and closing of the hydrogen bridge bonds is a dynamic process, we expected reaction 2 to be "slower" than the corresponding reaction of the terminal hydride species $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ with $B(C_6F_5)_3$ in ether (Scheme 1).[12] Indeed, reaction 2, which took several minutes to change color completely, was observed to be qualitatively slower than the reaction of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, which is too rapid to observe intermediates by NMR.

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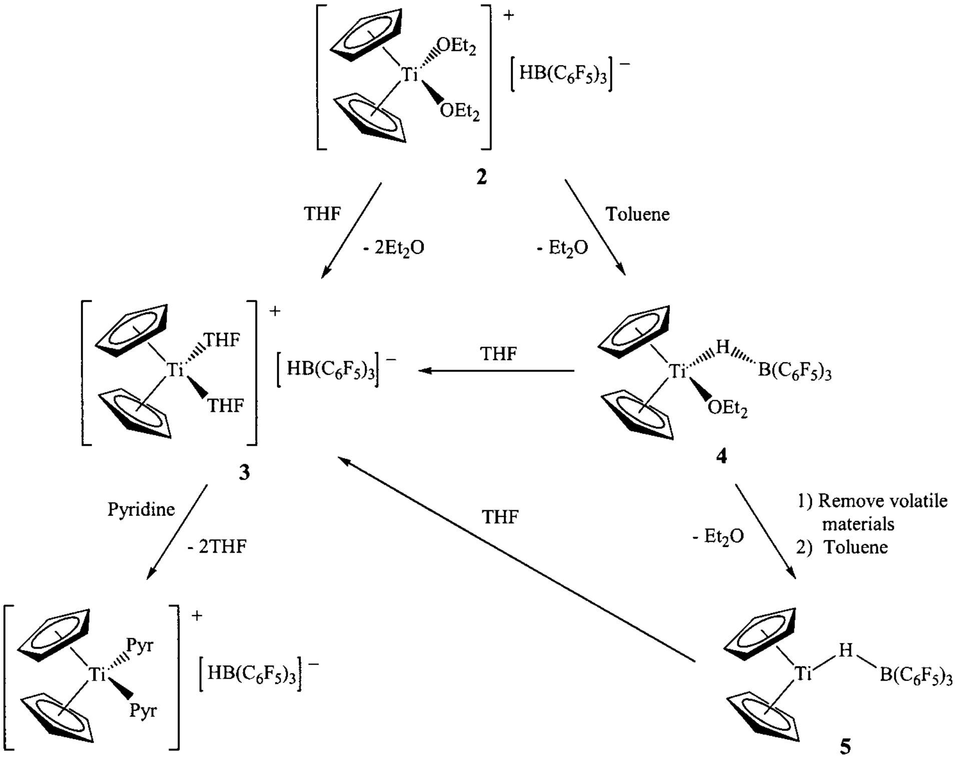
Scheme 4



Compounds **2** and **3** are more air sensitive than the titanocene organohydroborates $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$. Trials to obtain an IR spectrum of **2** with KBr did not succeed; apparently, **2** reacts with KBr during the preparation of the IR sample in the drybox to change color from blue to yellow. A Nujol mull was prepared instead. Light blue crystals of **2** and **3** were obtained from ether and a THF/hexane solution mixture, respectively. Crystals of **2** evolve ether under a nitrogen atmosphere at room temperature, turning dull blue in appearance. Pumping on **2** for even a short period of time also removes coordinated ether. Low carbon and hydrogen analyses for **2** substantiated the loss of ether. Consequently, yields of **2** from reaction 2 are not precise. This complication was not encountered with **3**. Salts **2** and **3** have characteristically different solubilities. Compound **2** is soluble in THF and toluene but is insoluble in ether, and **3** is soluble in THF and pyridine but is insoluble in ether and toluene.

Mononuclear titanocene (Ti(III)) salts with solvent ligands, such as **2** and **3**, are relatively rare, and to the best of our knowledge, no diethyl ether coordinated cations have been reported. Two of the earliest salts prepared were the acetonitrile and pyridine coordinated complexes $[Cp_2Ti(CH_3CN)_2][BPh_4]$[13] and $[Cp_2Ti(Pyr)_2][BPh_4]$.[13,14] The $[Cp_2Ti(CH_3CN)_2]^+$ cation was later prepared with the $[ZnCl_4]^-$ anion.[15] The mixed ligand species $[Cp_2Ti(CH_3CN)(THF)][BPh_4]$[16] and $[Cp_2Ti(OC_3H_6)(THF)]_2[Zn(B_{10}H_{12})_2]\cdot THF$[18] and the THF-coordinated compounds $[Cp_2Ti(THF)_2]$ $[BPh_4]$[14] and $[Cp_2Ti(THF)_2]$ $[Co(CO)_4]$[17] have also been synthesized.

Displacement Reactivity of 2. Through NMR spectroscopic studies, the ether molecules in **2** have been found to be weakly coordinated and labilized in toluene and THF (Scheme 4). In d_8-THF, the ether molecules are completely displaced from the cation to produce the THF coordinated salt, **3**. The ^{11}B NMR spectrum consists of a doublet at δ −25.5 that is consistent with the $[HB(C_6F_5)_3]^-$ anion. The only signals observed in the ^1H NMR spectrum are the multiplets associated with the free ether molecules. The cyclopentadienyl hydrogens are ^1H NMR silent due to the paramagnetism of the Ti(III) ion. Upon decoupling from ^{11}B, the $^1H\{^{11}B\}$ spectrum showed sharpening of a peak at 3.75 ppm corresponding to the hydride of the anion. Integration of this hydride resonance vs the free ether signals indicated that less than a molecule of ether remained. This is further confirmation for the lability of the coordinated ether under vacuum. Three sharp upfield resonances at −132.1, −165.4, and −167.7 ppm in the ^{19}F NMR spectrum correlate with the three inequivalent fluorines of the pentafluorophenyl rings of the anion. A comparable displacement reaction occurs when the cation in **3** is transformed into the disubstituted $[Cp_2Ti(Pyr)_2]^+$ cation by dissolution in pyridine.

When **2** is dissolved in d_8-toluene, remarkably no ^{11}B resonances are observed. The ^1H NMR spectrum at room temperature includes only two resonances due to the free ether, but these appear as broad unresolved signals rather than the expected multiplets. Increasing the temperature to 94 °C gradually resolved the ether resonances into sharp multiplets, without a change in the chemical shifts. Decreasing the temperature to −70 °C significantly broadened the resonances, without a substantial variation in the chemical shifts. Decoupling from ^{11}B did not affect the ^1H spectra. Two broad upfield resonances at −155.3 and −160.3 ppm for the *para*- and *meta*-fluorines, respectively, are apparent in the ^{19}F NMR spectrum at room temperature. Sharpening of these two resonances, without the appearance of new ones, was evident in the variable temperature ^{19}F NMR spectra at higher temperatures.

The preceding observations signify the interaction of the $[HB(C_6F_5)_3]^-$ anion with the paramagnetic Ti(III) ion. We propose that in toluene $[HB(C_6F_5)_3]^-$ displaces an ether molecule from the titanocene cation to form a covalent compound, $Cp_2Ti\{(\mu\text{-}H)B(C_6F_5)_3\}(OEt_2)$ (**4**), containing an unsupported hydrogen bridge (see Scheme 4). The absence of the ^{11}B and *ortho*-fluorine resonances and the appearance of the two broad ^{19}F singlets substantiate this formulation. Furthermore, a comparison of the ^{19}F NMR spectrum of **4** with **1** reveals that the chemical shifts of the *meta*- and *para*-fluorines are approximately the same. (The broad *meta*- and *para*-fluorine resonances of **1** and **4** are shifted downfield versus those of **2** and **3**.) This indicates that **4** must have structural features similar to those of **1**. The cyclopentadienyl protons, the bridging proton, and the coordinated ether protons are not detected because they are in close association with the paramagnetic Ti(III) ion.[26]

The coordinated ether on **4** is labile and is exchanging with the dissociated or free ether in solution, thus giving rise to the broad free ether resonances at room temperature. Since the protons on the coordinated ether are ^1H NMR silent, there is no apparent chemical shift averaging between the free and coordinated ether, that is, the chemical shifts of the free ether resonances are unvarying even though exchange is occurring. Increasing the temperature drives the dissociation until all of the coordinated ether has been completely dislodged to produce $Cp_2Ti\{(\mu\text{-}H)B(C_6F_5)_3\}$, **5** (Scheme 4). At 94 °C the exchange process has ceased and only free ether is present as evidenced by the distinctive ether multiplets. This phenomenon is supported by the ^{19}F NMR spectra. At room temperature the two *para*- and *meta*-fluorine resonances are broad due to ether exchange. At higher temperatures the resonances sharpen because the dynamic process has ceased and the fluorine nuclei experience only one magnetic environment in **5**.

Addition of THF to the NMR sample of **2** in toluene (Scheme 4) causes the broad ether resonances to resolve into their respective multiplets at room temperature and a doublet to appear in the ^{11}B NMR spectrum. The substitution of the last weakly coordinated ether by THF would take place initially followed by cleavage of the unsupported hydrogen bridge to afford **3**. This transformation validates that the anion has not been altered in toluene.

The variable temperature NMR experiment demonstrated that the monocoordinated ether ligand of **4** is labile. It is therefore not surprising that the ether ligand is eliminated under vacuum by the following procedure (Scheme 4). When complex **2** is twice dissolved in toluene proceeded by removal of the volatile materials under vacuum and the resulting blue solid is dissolved in d_8-toluene, ^1H and ^{11}B NMR spectra are silent. These spectra reveal that all of the free ether has been removed and suggest that the $[HB(C_6F_5)_3]^-$ anion is in intimate contact with the Ti(III) ion through an unsupported hydrogen bridge. The ^{19}F NMR spectrum still contains only two broad signals at −155.2 and −160.2 ppm, which are identical to the chemical shifts of **4**. Although X-ray quality crystals could not be obtained due to the extremely air-sensitive nature of the species, the NMR evidence and elemental analyses point to a system that is formulated as $Cp_2Ti\{(\mu\text{-}H)B(C_6F_5)_3\}$ (**5**), having an open coordination site on titanium. This would constitute an uncommon but precedented 15-electron configuration for the Ti(III) ion.[27] Complex **5** is converted into **3** by addition of THF (Scheme 4). There are no ether resonances in the ^1H NMR spectrum, which is further confirmation for the complete removal of the coordinated ether by vacuum.

It was speculated that one of the fluorine atoms from a pentafluorophenyl ring might donate a lone pair of electrons to form a σ-bond with titanium to displace the remaining coordinated ether in **4** or fill the vacant coordination site in **5**. Such σ-donation from fluorine atoms on $B(C_6F_5)_3$ to zirconium[11a,28] and titanium[29] has been noted previously. However, the simplicity of the solution ^{19}F NMR spectra dismisses this hypothesis.

As with **2** and **3**, the substitution of the solvent ligands by nucleophiles has been documented with the acetonitrile complex $[Cp_2Ti(CH_3CN)_2]$ $[BPh_4]$. Recrystallization of this salt in pyridine resulted in the disubstituted cation $[Cp_2Ti(Pyr)_2]^+$,[13] and in THF the monosubstituted cation $[Cp_2Ti(CH_3CN)(THF)]^+$ [16] was isolated. Cationic titanocene phosphines with the formulations $[Cp_2Ti(CH_3CN)(PMe_3)]^+$ and $[Cp_2Ti(PMe_3)_2]^+$ were also prepared from $[Cp_2Ti(CH_3CN)_2]$ $[BPh_4]$.[15] Substitution of the THF ligands in $[Cp_2Ti(THF)_2]$ $[BPh_4]$ occurred in the presence of pyridine to yield the cation, $[Cp_2Ti(Pyr)_2]^+$.[14]

Hydride Ion Abstraction from $Cp_2Ti\{(\mu\text{-}H)_2B(C_6F_5)_2\}$, 1. Compared to the organohydroborates $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8, C_5H_{10}, C_8H_{14}$), the bridging hydrogens of **1** should be less Lewis basic because of the electron-withdrawing effect of the pentafluorophenyl groups. Therefore, it was of interest to test abstraction of the bridging hydrogens in **1** by $B(C_6F_5)_3$ in coordinating and noncoordinating solvents. The metathesis product **1** is soluble in THF and hydride ion abstraction proceeded in a facile manner to afford **3** (reaction 3). The organoborane product of reaction 3 is perceived to be the THF adduct of $HB(C_6F_5)_2$ on the basis of the resonance at −0.7 ppm in the ^{11}B NMR spectrum.[30] The rate of hydride ion abstraction from **1** compared to the titanocene organohydroborates appeared to be about the same order of magnitude despite the lower basicity of the bridging hydrogens. Hydride ion abstraction was not observed in diethyl ether due to the insolubility of **1** in that solvent. Likewise, abstraction did not occur in toluene even after heating at 70 °C for 24 h.

Molecular Structures of 1, 2, and 3. The molecular structures of **1**, **2**, and **3** were determined by single-crystal X-ray diffraction analysis. Structures of **2** and **3** are shown in Figures 1 and 2. Crystallographic data,

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(26) The paramagnetism of the Ti(III) ion has been shown to affect nuclei as far as four and five bonds away. Consequently, nuclei that are in close vicinity to the Ti(III) ion are typically NMR silent. See ref 4 and NMR spectral data for $Cp_2Ti\{(\mu\text{-}H)_2B(C_6F_5)_2\}$, **1**.

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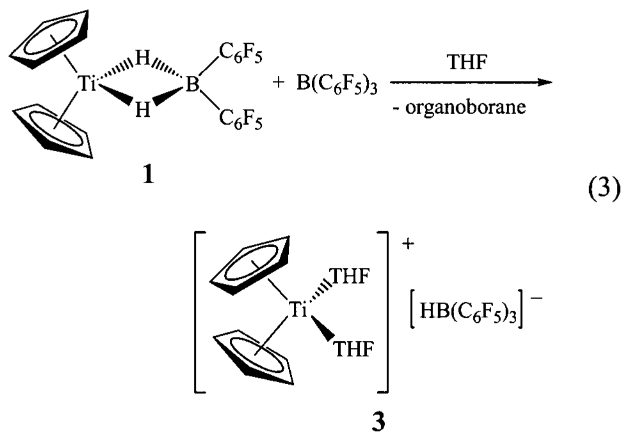
(30) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492.



(3)

bond distances, and bond angles are given in Tables 1 and 2. Previously, the molecular structure of **1** was determined by both Piers et al.[3a] and Douthwaite[3b] and consequently, molecular structures, bond distances, and angles are included only in the Supporting Information. There are three unique molecules in the asymmetric unit cell of **2**. Since the cations in these independent molecules of **2** are comparable, only the molecular structure of one cation is shown.

The Ti- -B distances (2.433(4), 2.418(4) Å) in **1** determined by this laboratory are in agreement with those of Piers et al. (2.450(10), 2.428(9) Å)[3a] and Douthwaite (2.440(3), 2.454(3) Å).[3b] These Ti- -B distances are generally longer than for $Cp_2Ti\{(\mu\text{-}H)_2BH_2\}$ (2.37(1) Å)[2c] and the titanocene organohydroborates $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, 2.409(4) Å; C_5H_{10}, 2.446(3) Å; C_8H_{14}, 2.428(2) Å).[4] This lengthening of the Ti- -B distance is attributed to the electron-withdrawing pentafluorophenyl rings.

The molecular structures of **2** and **3** are similar to each other. The coordination geometry about the titanium center is best described as a distorted tetrahedron. Occupying the corners of the tetrahedron are the centers of the two cyclopentadienyl rings and the two oxygen atoms of the ether and THF molecules. The Ti−O bond distances range from 2.231(3) to 2.275(3) Å in **2**, and the distances are 2.199(1) and 2.223(2) for **3**. It is not surprising that **3** has shorter Ti−O distances because THF is a stronger Lewis base than ether. This trend is consistent with other titanocene cations coordinated to THF, such as $[Cp_2Ti(CH_3CN)(THF)]\,[BPh_4]$ (2.175(4) Å),[16] $[Cp_2Ti(THF)_2]\,[Co(CO)_4]$ (2.190(5) to 2.219(6) Å),[17] and $[Cp_2Ti(OC_3H_6)(THF)]_2\,[Zn(B_{10}H_{12})_2]\cdot THF$ (2.21(1) and 2.13(1) Å).[18] The O−Ti−O bond angles are 82.39(9), 83.5(1), and 79.5(1)° in **2** and 78.36(5)° in **3**. These are comparable to the cations in $[Cp_2Ti(THF)_2]\,[Co(CO)_4]$ (77.2(2) to 82.9(2)°)[17] and $[Cp_2Ti(OC_3H_6)(THF)]_2\,[Zn(B_{10}H_{12})_2]\cdot THF$ (76.9 and 78.6°).[18] The structural features of the $[HB(C_6F_5)_3]^-$ anions are not extraordinary (see Table 2 and refs 11a and 12).

Experimental Section

General Comments. All manipulations were carried out on a standard high vacuum line or in a drybox under an atmosphere of nitrogen. Diethyl ether, tetrahydrofuran, and toluene were dried over sodium/benzophenone and freshly distilled prior to use. Hexane was stirred over concentrated sulfuric acid for 2 days and then decanted and washed with water. Next, the hexane was stirred over calcium hydride for 6 days, decanted and stirred over sodium/benzophenone for 5 days, and finally distilled into a storage bulb containing sodium/benzophenone. $B(C_6F_5)_3$ was purchased from Aldrich and used as received. $B(C_6F_5)_3$ was also received as a gift from Dr. John Lee of Albemarle Corp. The titanocene organohydroborates $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8, C_5H_{10}, C_8H_{14}$) were prepared by literature procedures.[4] Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Proton spectra (δ(TMS) 0.00 ppm) were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 MHz and on a Bruker DPX-400 NMR spectrometer operating at 400.13 MHz. Boron-11 spectra (externally referenced to $BF_3\cdot OEt_2$ (δ 0.00 ppm)) were recorded at 128.38 or 80.25 MHz as noted. Fluorine-19 spectra (externally referenced to $CFCl_3$ (δ 0.00 ppm)) were recorded at 235.33 MHz. Infrared spectra were recorded on a Mattson Polaris Fourier Transform spectrometer with 2 cm^{-1} resolution.

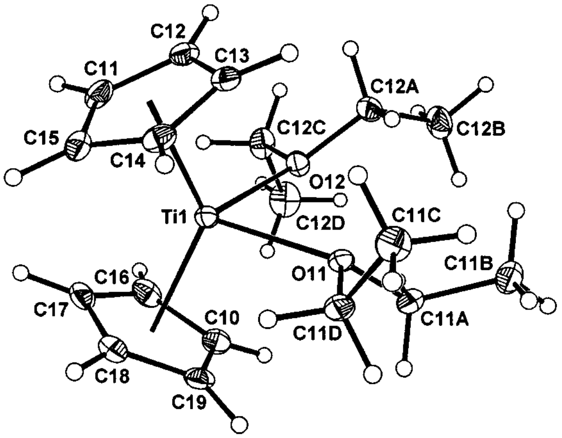


Figure 1. Molecular structure of the cation in $[Cp_2Ti(OEt_2)_2]\,[HB(C_6F_5)_3]$, **2**, showing 15% probability thermal ellipsoids. Hydrogens attached to carbon atoms are shown with arbitrary thermal ellipsoids.

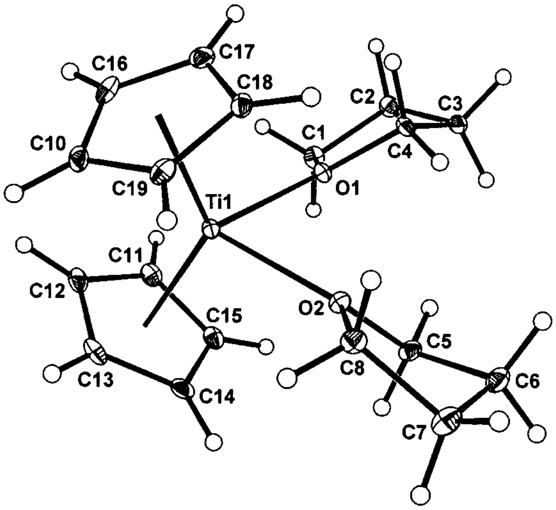


Figure 2. Molecular structure of the cation in $[Cp_2Ti(THF)_2][HB(C_6F_5)_3]$, **3**, showing 15% probability thermal ellipsoids. Hydrogens attached to carbon atoms are shown with arbitrary thermal ellipsoids.

X-ray Structure Determination. Single-crystal X-ray diffraction data were collected using graphite-monochromated Mo Kα radiation on a Nonius KappaCCD diffraction system. Single crystals of **1**, **2**, and **3** were mounted on the tip of a glass fiber coated with Fomblin oil (a perfluoro polyether). Crystallographic data was collected at −70 °C for **1**, −80 °C for **2**, and −123 °C for **3**. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and

Table 1. Crystal and Structure Refinement Data for 1, 2, and 3

	1	**2**	**3**
empirical formula	$C_{44}H_{24}B_2F_{20}Ti_2$	$C_{108}H_{93}B_3F_{45}O_6Ti_3$	$C_{36}H_{27}BF_{15}O_2Ti$
formula wt. (amu)	1050.05	2517.95	835.29
T (°C)	-70	-80	-123
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	11.583(1)	14.879(1)	11.284(1)
b (Å)	12.634(1)	52.512(2)	13.584(1)
c (Å)	15.697(1)	14.915(1)	22.592(1)
α (deg)	90.62(1)		
β (deg)	109.47(1)	114.85(1)	102.52(1)
γ (deg)	110.54(1)		
V (Å^3)	2006.7(3)	10574(1)	3380.7(4)
Z	4	12	4
density (calcd, g cm^{-3})	1.738	1.582	1.641
μ (mm^{-1})	0.527	0.356	0.371
crystal size (mm)	0.12 × 0.15 × 0.15	0.31 × 0.38 × 0.38	0.12 × 0.27 × 0.38
θ range (deg)	2.38−25.06	2.33−25.03	2.31−24.99
index ranges	$-13 \leq h \leq 13$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$	$-17 \leq h \leq 17$ $-62 \leq k \leq 62$ $-17 \leq l \leq 17$	$-13 \leq h \leq 13$ $-16 \leq k \leq 15$ $-26 \leq l \leq 26$
reflections collected	14 090	61 834	19 006
independent reflections	7080	18 594	5924
R_{int}	0.0329	0.0509	0.0442
completeness to θ	99.5%	99.6%	99.7%
max/min transmission	0.9395, 0.9252	0.8976, 0.8766	0.9568, 0.8719
data/restraints/parameters	7080/0/629	18 594/0/1624	5924/0/500
goodness-of-fit on F^2	1.078	1.031	1.011
final R indices [$I \geq 2.0\sigma(I)$]^{a,b}	$R_1 = 0.0526$, w$R_2 = 0.1232$	$R_1 = 0.0663$, w$R_2 = 0.1563$	$R_1 = 0.0377$, w$R_2 = 0.0778$
R indices (all data)	$R_1 = 0.0779$, w$R_2 = 0.1323$	$R_1 = 0.1235$, w$R_2 = 0.1799$	$R_1 = 0.0656$, w$R_2 = 0.0857$
largest diff. peak and hole (e Å^{-3})	0.484 and −0.346	1.178 and −0.385	0.247 and −0.250

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} w$R_2 = \{\sum w(F_o2 - F_c2)^2/\sum w(F_o2)^2\}^{1/2}$.

Table 2. Selected Bond Distances and Angles for 2 and 3

compound **2**		compound **3**	
	Bond Lengths (Å)		
ave Ti(1)−C(11−15)	2.386	ave Ti(1)−C(11−15)	2.382
ave Ti(1)−C(16−10)	2.382	ave Ti(1)−C(16−10)	2.379
Ti(1)−O(11)	2.260(2)	Ti(1)−O(1)	2.199(1)
Ti(1)−O(12)	2.262(2)	Ti(1)−O(2)	2.223(2)
B(1)−H(1)	1.15(4)	B(1)−H(1)	1.12(2)
	Bond Angles (deg)		
O(11)−Ti(1)−O(12)	82.39(9)	O(1)−Ti(1)−O(2)	78.36(5)
Ti(1)−O(11)-C(11A)	121.0(2)	Ti(1)−O(1)−C(1)	125.3(1)
Ti(1)−O(11)-C(11D)	116.2(2)	Ti(1)−O(1)−C(4)	124.8(1)
Ti(1)−O(12)-C(12A)	121.3(2)	Ti(1)−O(2)−C(5)	125.2(1)
Ti(1)−O(12)-C(12C)	118.2(2)	Ti(1)−O(2)−C(8)	124.2(1)

corrected for Lorentz and polarization effects using DENZO.[31] The empirical absorption correction was applied with SORTAV.[32] Structures of **1**, **2**, and **3** were solved by direct methods and refined using SHELXTL (difference electron density calculations and full matrix least-squares refinements).[33] For each structure, non-hydrogen atoms were located and refined anisotropically. For **2** and **3** the terminal hydrogen atoms of the $[HB(C_6F_5)_3]^-$ anions and the bridging hydrogens of **1** were located and refined isotropically. All other hydrogen atoms were calculated and fixed during the refinement. There are two independent molecules in the asymmetric unit cell of **1**. For complex **2**, the $[HB(C_6F_5)_3]^-$ anions of two independent molecules are disordered in the fluorine atom positions.

Preparation of $Cp_2Ti\{(\mu\text{-}H)_2B(C_6F_5)_2\}$, 1. A. From $Cp_2Ti\{(\mu\text{-}H)_2BC_4H_8\}$. A 50 mL flask was charged with 108 mg (0.437 mmol) of $Cp_2Ti\{(\mu\text{-}H)_2BC_4H_8\}$ and 227 mg (0.443 mmol) of $B(C_6F_5)_3$. Approximately 20 mL of toluene was condensed into the flask at −78 °C. The flask was warmed to room temperature and stirred for 2 h. The ^{11}B NMR spectrum (80 MHz) of the reaction solution showed the formation of an organoborane ($B(C_6F_5)(C_4H_8)$, δ 81.8 (br s)). The solvent was removed under vacuum, and the solid was washed with a 1:1 toluene/hexane mixture until the washings were colorless. The resulting purple solid was dried under vacuum for 2 h, and 131 mg (57.0%) of **1** was isolated. Crystals of **1** were grown from toluene by slowly evapoartating the solvent at room temperature. ^1H NMR (250 MHz, C_6D_6): silent. ^{11}B NMR (80 MHz, C_6D_6): silent. ^{19}F NMR (235 MHz, C_6D_6): δ −154.3 (br s, 1F, *p*-F), −161.7 (br s, 2F, *m*-F). IR (Nujol mull): 3137 (w, br), 2730 (vw), 2129 (w), 2074 (m), 2008 (m), 1900 (w), 1829 (vw), 1645 (m), 1514 (s), 1401 (m), 1285 (m), 1178 (w), 1105 (s), 1093 (s), 1022 (m), 966 (s), 910 (m), 899 (m), 843 (w), 813 (s), 803 (s), 763 (m), 731 (w), 722 (w), 674 (w), 628 (w), 606 (w), 568 (w) cm^{-1}. Anal. Calcd for $C_{22}H_{12}TiBF_{15}$: C, 50.33; H, 2.30. Found: C, 49.91; H, 2.31.

B. From $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$. The preparation of **1** (86 mg, 68% yield) by reaction of $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ (63 mg, 0.24 mmol) and $B(C_6F_5)_3$ (126 mg, 0.246 mmol) was similar to that described above in A. The ^{11}B NMR spectrum (80 MHz) of the reaction solution showed the formation of an organoborane ($B(C_6F_5)(C_5H_{10})$, δ 82.7 (br s)).

C. From $Cp_2Ti\{(\mu\text{-}H)_2BC_8H_{14}\}$. The preparation of **1** (252 mg, 68.1% yield) by reaction of $Cp_2Ti\{(\mu\text{-}H)_2BC_8H_{14}\}$ (211 mg, 0.700 mmol) and $B(C_6F_5)_3$ (359 mg, 0.701 mmol) was similar to that described above in A. The ^{11}B NMR spectrum (80 MHz) of the reaction solution displayed the appearance of an organoborane ($B(C_6F_5)(C_8H_{14})$, δ 85.0 (br s)). A GC-MS analysis of the reaction solution verified the product, $B(C_6F_5)(C_8H_{14})$. GC-MS (EI): calcd for $C_{14}H_{14}BF_5$, m/z = 288.1; obsd, m/z = 288.1.

Preparation of $[Cp_2Ti(OEt_2)_2]$ $[HB(C_6F_5)_3]$, 2. A. From $Cp_2Ti\{(\mu\text{-}H)_2BC_4H_8\}$. A 194 mg (0.785 mmol) quantity of $Cp_2Ti\{(\mu\text{-}H)_2BC_4H_8\}$, 402 mg (0.785 mmol) of $B(C_6F_5)_3$, and 20 mL of diethyl ether were charged into a 50 mL flask. After stirring for 1 h, the ^{11}B NMR spectrum (80 MHz) of the reaction solution showed the appearance of the organodiborane, $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$ (δ 28.5 (br t)). The solution was concentrated to

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(31) Otwinowsky, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, Eds., R. R.; Academic Press: New York, 1997; pp 307−326.

(32) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(33) SHELXTL (version 5.10), Bruker Analytical X-ray Systems, 1997.

5 mL and light blue crystals formed. The crystals were washed with a 1:1 ether/hexane mixture until the washings were colorless. The crystals were dried under vacuum for 30 min. Complex **2** was isolated as a powder blue solid (446 mg, 67.7% yield). IR (Nujol mull): 3120 (vw), 2730 (vw), 2384 (w), 2348 (w), 2159 (vw), 2034 (vw), 1642 (m), 1604 (w), 1550 (w), 1513 (s), 1306 (w), 1272 (m), 1218 (vw), 1177 (w), 1113 (ms), 1105 (ms), 1071 (m), 1037 (m), 1013 (m), 962 (s), 945 (m, sh), 928 (w), 905 (m), 844 (w), 822 (s), 806 (m, sh), 786 (m), 760 (m), 722 (m), 670 (vw), 658 (w), 646 (w), 603 (w), 569 (w) cm^{-1}. Anal. Calcd for $C_{36}H_{31}TiO_2BF_{15}$: C, 51.52; H, 3.72. Found: C, 48.86; H, 2.60.[34]

B. From $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$. The preparation of **2** (663 mg, 79.0% yield) by reaction of $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ (261 mg, 1.00 mmol) and $B(C_6F_5)_3$ (512 mg, 1.00 mmol) was similar to that described above in A. The ^{11}B NMR spectrum (80 MHz) of the reaction solution displayed the appearance of an unidentified organoborane (δ 53.7 (br s)).

C. From $Cp_2Ti\{(\mu\text{-}H)_2BC_8H_{14}\}$. The preparation of **2** (294 mg, 59.3% yield) by reaction of $Cp_2Ti\{(\mu\text{-}H)_2BC_8H_{14}\}$ (178 mg, 0.591 mmol) and $B(C_6F_5)_3$ (317 mg, 0.619 mmol) was similar to that described above in A. The ^{11}B NMR spectrum (80 MHz) of the reaction solution displayed the appearance of an unidentified organoborane (δ 56.2 (br s)).

Formation of $[Cp_2Ti(d_8\text{-THF})_2][HB(C_6F_5)_3]$, 3, from 2. Approximately 20 mg of **2** was dissolved in d_8-THF in an NMR tube that was flame-sealed. $^1H\{^{11}B\}$ NMR (400 MHz, d_8-THF): δ 3.75 (br s, 1H, HB), 3.38 (q, $^3J_{HH} = 7.0$ Hz, 3.6 H, free ether), 1.04 (t, $^3J_{HH} = 7.0$ Hz, 4.7 H, free ether). ^{11}B NMR (128 MHz, d_8-THF): δ −25.5 (d, $^1J_{BH} = 90$ Hz). ^{19}F NMR (235 MHz, d_8-THF): δ −132.1 (br d, 2F, *o*-F), −165.4 (br t, 1F, *p*-F), −167.7 (br t, 2F, *m*-F).

Formation of $Cp_2Ti\{(\mu\text{-}H)B(C_6F_5)_3\}(OEt_2)$, 4, from 2. Approximately 20 mg of **2** was dissolved in d_8-toluene in an NMR tube that was flame-sealed. ^{1}H NMR (400 MHz, d_8-toluene): δ 3.32 (br s, 2H, free ether), 1.05 (br s, 3 H, free ether). ^{11}B NMR (80 MHz, d_8-toluene): silent. ^{19}F NMR (235 MHz, d_8-toluene): δ −155.3 (v br s, 1F, *p*-F), −160.3 (v br s, 2F, *m*-F).

Conversion of 4 into 3. Several drops of d_8-THF were added to a solution of **2** in d_8-toluene. The NMR tube was flame-sealed. ^{1}H NMR (400 MHz, d_8-toluene, d_8-THF): δ 3.33 (q, $^3J_{HH} = 7.0$ Hz, 2 H, free ether), 1.14 (t, $^3J_{HH} = 7.0$ Hz, 3 H, free ether). The *H*B proton resonance was not observed in the ^{1}H NMR spectrum because it appears as a broad quartet overlapping the most downfield d_8-THF resonance. ^{11}B NMR (128 MHz, d_8-toluene, d_8-THF): δ −24.9 (d, $^1J_{BH} = 86$ Hz). ^{19}F NMR (235 MHz, d_8-toluene, d_8-THF): δ −131.2 (br d, 2F, *o*-F), −163.8 (br t, 1F, *p*-F), −166.3 (br t, 2F, *m*-F).

Formation of $Cp_2Ti\{(\mu\text{-}H)B(C_6F_5)_3\}$, 5, from 2. In an NMR tube, **2** was dissolved in toluene followed by removal of the volatile materials on the vacuum line for 15 min. This step was repeated again with final dissolution of the blue solid in d_8-toluene. The NMR tube was flame-sealed. ^{1}H NMR (250 MHz, d_8-toluene): silent. ^{11}B NMR (80 MHz, d_8-toluene): silent. ^{19}F NMR (235 MHz, d_8-toluene): δ −155.2 (v br s, 1F, *p*-F), −160.2 (v br s, 2F, *m*-F). IR (Nujol mull): 3124 (vw), 2724 (vw), 2153 (m), 2115 (m), 2033 (m, br), 1984 (m), 1953 (m), 1643 (s), 1606 (w), 1518 (s), 1279 (s), 1179 (vw), 1098 (s, br), 1024 (s), 1009 (s, br), 971 (s, br), 945 (s), 915 (ms), 894 (ms), 820 (s, br), 787 (ms), 770 (ms), 759 (ms), 727 (ms), 694 (w), 686 (w), 669 (m), 654 (m), 641 (m), 611 (w), 601 (w), 569 (w) cm^{-1}. Anal. Calcd for $C_{28}H_{11}TiBF_{15}$: C, 48.67; H, 1.60. Found: C, 48.77; H, 1.93.

Conversion of 5 into 3. In an NMR tube, **2** was dissolved in toluene followed by removal of the volatile materials on the vacuum line for 15 min. This step was repeated again with final dissolution of the blue solid (**5**) in d_8-THF. The NMR tube was flame-sealed. ^{1}H NMR (400 MHz, d_8-THF): silent. (The *H*B proton was not observed in the ^{1}H NMR.) ^{11}B NMR (128 MHz, d_8-THF): δ −25.1 (d, $^1J_{BH} = 86$ Hz). ^{19}F NMR (235 MHz, d_8-THF): δ −132.0 (br d, 2F, *o*-F), −164.8 (br t, 1F, *p*-F), −167.6 (br t, 2F, *m*-F).

Preparation of $[Cp_2Ti(THF)_2]$ $[HB(C_6F_5)_3]$, 3. A 50 mL flask was charged with 110 mg (0.421 mmol) of $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ and 216 mg (0.422 mmol) of $B(C_6F_5)_3$. Approximately 20 mL of THF was condensed into the flask at −78 °C. The flask was warmed to room temperature and stirred for 1 h. The ^{11}B NMR spectrum (80 MHz) of the reaction solution indicated the presence of an organoborane (δ 54.0 (br s)). The solvent was reduced under vacuum to about 5 mL, and dry hexane was added to produce a blue oil phase. The solution was decanted from the oil. The oil was dissoved in a minimum amount of THF followed by addition of hexane. Recrystallization was repeated until blue crystals formed. The crystals were dried under vacuum for 30 min producing 285 mg (81.0% yield) of **3**. $^1H\{^{11}B\}$ NMR (400 MHz, d_8-THF): $\delta \sim 3.65$ (br s, shoulder of the most downfield d_8-THF resonance, *H*B). ^{11}B NMR (128 MHz, d_8-THF): δ −25.3 (d, $^1J_{BH} = 86$ Hz). ^{19}F NMR (235 MHz, d_8-THF): δ −131.9 (br d, 2F, *o*-F), −165.2 (br t, 1F, *p*-F), −167.5 (br t, 2F, *m*-F). IR (KBr): 3128 (vw), 3001 (w), 2910 (vw), 2885 (vw), 2406 (w), 2381 (vw, sh), 1641 (w), 1510 (s), 1464 (vs), 1379 (w), 1276 (m), 1106 (m), 1074 (m), 1027 (m), 1014 (m), 970 (s), 902 (w), 861 (w), 816 (m), 807 (m), 760 (w), 726 (w), 673 (w), 678 (w), 601 (w), 567 (w) cm^{-1}. Anal. Calcd for $C_{36}H_{27}TiO_2BF_{15}$: C, 51.77; H, 3.26. Found: C, 51.40; H, 3.17.

Conversion of 3 into $[Cp_2Ti(d_5\text{-Pyr})_2]$ $[HB(C_6F_5)_3]$. About 20 mg of **3** was dissolved in d_5-pyridine producing an olive green solution. ^{1}H NMR (400 MHz, d_5-pyridine): $\delta \sim 4.6$ (br q, $^1J_{BH} = 91$ Hz, 1 H, *H*B), 3.64 (br s, 8 H, free THF), 1.61 (br s, 8 H, free THF). $^1H\{^{11}B\}$ NMR (d_5-pyridine): δ 4.65 (br s, 1H, *H*B). ^{11}B NMR (128 MHz, d_5-pyridine): δ −25.0 (d, $^1J_{BH} = 91$ Hz). ^{19}F NMR (235 MHz, d_5-pyridine): δ −129.9 (br d, 2F, *o*-F), −161.0 (br t, 1F, *p*-F), −163.9 (br t, 2F, *m*-F).

Formation of 3 from 1. A 50 mL flask was charged with 115 mg (0.219 mmol) of **1** and 117 mg (0.229 mmol) of $B(C_6F_5)_3$. About 20 mL of THF was condensed into the flask at −78 °C. The flask was warmed to room temperature and stirred for 2 h. The ^{11}B NMR spectrum (80 MHz) of the reaction solution indicated the presence of an organoborane THF adduct (δ −0.7 (br d)). The volume of the solution was reduced under vacuum to approximately 5 mL and a blue oil phase formed upon addition of hexane. Isolation of **3** (128 mg, 74.4%) was performed in the same manner as described in the preparation of **3**. ^{1}H NMR (400 MHz, d_5-pyridine): $\delta \sim 4.6$ (br q, $^1J_{BH} = 91$ Hz, 1 H, *H*B), 3.65 (br s, 8 H, free THF), 1.63 (br s, 8 H, free THF). ^{11}B NMR (128 MHz, d_5-pyridine): δ −23.7 (d, $^1J_{BH} = 86$ Hz).

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Supporting Information Available: Molecular structures of the two independent molecules of **1**; molecular structures of the two other independent cations and three independent anions of **2**; molecular structure of the anion of **3**; tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **1**, **2**, and **3**; relevant ^{1}H, ^{11}B, and ^{19}F NMR spectra. Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[34] See text for an explanation of the low carbon and hydrogen analyses.